



## Review

## Recent progress in doped carbon nanomaterials as effective cathode catalysts for fuel cell oxygen reduction reaction

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## H I G H L I G H T S

- This review systematically summarizes recent achievements in heteroatom doped carbon materials as ORR catalysts.
- Some novel NPMCs with excellent electrocatalytic performance toward ORR are presented.
- Some problems and prospects involving doped carbon materials as ORR catalysts are discussed.

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## A B S T R A C T

The fuel cell (FC), as a clean and high-efficiency device, has drawn a great deal of attention in terms of both fundamentals and applications. However, the high cost and scarcity of the requisite platinum catalyst as well as a sluggish oxygen reduction reaction (ORR) at the cathode in FC have become the greatest barrier to large-scale industrial application of FC. The development of novel non-precious metal catalysts (NPMC) with excellent electrocatalytic performance has been viewed as an important strategy to promote the development of FC. Recent studies have proven that metal free carbon materials doped with heteroatom (e.g. N, B, P, S or Se) have also shown striking electrocatalytic performance for ORR and become an important category of potential candidates for replacing Pt-based catalysts. This review summarizes recent achievements in heteroatom doped carbon materials as ORR catalysts, and will be beneficial to future development of other novel low-cost NPMCs with high activities and long lifetimes for practical FC applications.

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## 1. Introduction

The development of alternative and green energy sources has become an urgent research topic due to ever increasing global energy depletion and the environmental impact of traditional energy resources [1,2]. The fuel cell (FC), a clean and high-efficiency device that directly converts chemical energy from a fuel into electricity through chemical reaction with oxygen or another oxidizing agent, has drawn a great deal of attention in terms of both fundamentals and applications [3–5]. Pt-based materials are known to be the most active catalysts for oxygen reduction reaction (ORR) at the cathode in FCs. However, despite the considerable research efforts in Pt-based catalysts, large-scale commercialization is still restricted mainly by their high cost, poor durability and slow electron-transfer kinetics [6]. Long-term efforts to reduce or

replace Pt-based catalysts have been performed [7–9]. In particular, the development of novel non-precious metal catalysts (NPMC), which exhibit both high activity and practical durability, has been considered one of the most active and competitive fields in chemistry and materials science [8]. Since Jasinski [10] first observed that cobalt phthalocyanine was able to catalyze the oxygen reduction reaction (ORR), various NPMC materials [11–14] including N-coordinated transition metal (TM) macromolecules, chalcogenides, oxynitrides, carbonitrides, and TM-doped conductive polymers have been evaluated as potential substitutes for Pt-based catalysts. Among these candidates, nitrogen-doped carbon materials in particular (e.g., carbon nanotubes, nanotube cups, ordered mesoporous graphitic arrays, and graphene) [15–22] have drawn much attention due to their excellent electrocatalytic activities as well as low cost, good durability, and environmental friendliness, which opens the way to the preparation of a new class of metal-free catalysts for ORR. Very recently, graphitic materials doped with other heteroatoms, such as P-doped graphite layers [23] and B-doped carbon nanotubes [24], have also been developed

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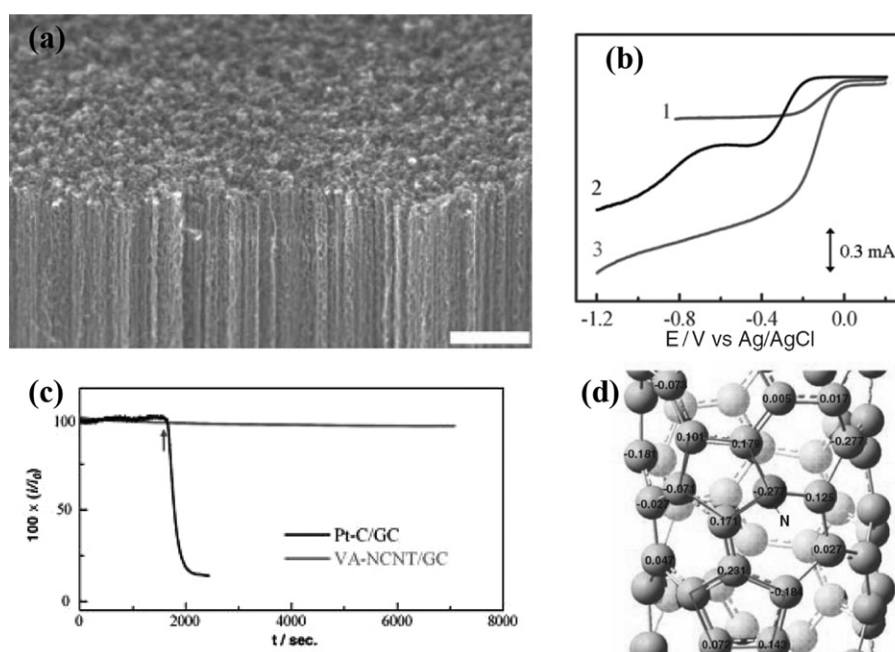
and shown to possess pronounced catalytic activity for ORR. Our recent efforts have revealed that sulfur (selenium or iodine) doping also improves the electrocatalytic performance of graphite materials [25–27]. As a rising category of potential candidates for the replacement of Pt-based catalysts, heteroatom doped graphite materials are considered to have great potential to solve some of the vital issues in the field of fuel cells and are expected to contribute to sustainable energy generation system devices. Recent rapid increases in the number of investigations on doped carbon materials have motivated demand for reviewing of this research field. To our knowledge, although some investigations or short reviews involving heteroatom doped graphite materials as ORR catalysts for application in fuel cells have been reported [28], comprehensive reviews are still rare. This review summarizes recent achievements in heteroatom doped carbon materials as ORR catalysts, and will be beneficial to future development of other novel low-cost NPMCs with high activities and long lifetimes for practical FC applications.

## 2. Doped carbon nanomaterials as ORR electrocatalysts

### 2.1. N-doped carbon nanomaterials as ORR catalysts

In the several decades since Jasinski reported for the first time that transition metal porphyrins and phthalocyanines have electrocatalytic activity toward ORR [10], pyrolysis of transition metal, carbon, and nitrogen-containing precursors at high temperature has become the general method for obtaining NPMCs with high ORR activity. Some researchers have proposed that the electrocatalytic activity observed in these NPMCs may be attributable to the presence of a C–N–M (M = Fe, Co or Ni) structure [6,29]. However, Dai's group [15] has recently found that vertically aligned nitrogen-doped carbon nanotubes (VA-NCNTs, Fig. 1a) produced by pyrolysis of iron phthalocyanine could also act as extremely effective metal-free ORR electrocatalysts, even after complete removal of the residual Fe catalyst by electrochemical purification. In

alkaline electrolytes, the metal-free VA-NCNTs exhibit a much higher catalytic activity ( $4.1 \text{ mA cm}^{-2}$  vs.  $1.1 \text{ mA cm}^{-2}$ ), lower overpotential (Fig. 1b) and better long-term operation stability compared to commercially available Pt/carbon black catalysts (20% platinum on VulcanXC-72R; E-TEK). Moreover, the crossover test (Fig. 1c) demonstrated that the VA-NCNT electrode was insensitive to CO poisoning even after adding about 10% CO in oxygen. To the best of our knowledge, these electrocatalytic performances (e.g., ORR activity, stability and overpotential) of the VA-NCNTs can be comparable to those of other non-noble metal catalysts (e.g., Ni, Co and spinel manganese–cobalt oxide) [30,31] in an alkaline electrolyte. This discovery quickly motivated much interest in developing new metal-free catalysts with more realistic value for fuel cell applications. Recently, various metal-free N-doped carbon materials with striking electrocatalytic performance for ORR have been developed and become an important category of potential candidates for replacing Pt-based catalysts [15–22]. According to Dai's proposal based on quantum mechanics calculations with B3LYP hybrid density functional theory (Fig. 1d), the reported high activity for metal free N-doped carbon materials is likely attributable to the strong electronic affinity of N atoms and substantially high positive charge density on the adjacent C atoms resulting in very favorable adsorption of  $\text{O}_2$ . This parallel diatomic adsorption may effectively weaken O–O bonding and facilitate the direct reduction of oxygen to  $\text{OH}^-$  via a four-electron process [15]. However, there is still some controversy concerning the activity enhancement mechanism because it is difficult to completely remove the catalyst particles that become encapsulated in graphite frameworks and these metal particles may potentially affect ORR performance. The development of truly metal-free N-doped carbon materials with excellent ORR catalytic activity is therefore of both scientific and practical significance [32–34]. Liu et al. reported the successful fabrication of nitrogen-doped ordered mesoporous graphitic arrays (NOMGAs) by a metal-free nanocasting technique using nitrogen-containing aromatic dyes as the carbon precursors. The properties of the resulting NOMGAs were superior to those



**Fig. 1.** (a) SEM image of the as-synthesized VA-NCNTs on a quartz substrate. Scale bars, 2  $\mu\text{m}$ . (b) Rotating ring-disk electrode (RRDE) voltammograms for oxygen reduction in air-saturated 0.1 M KOH at the Pt-C/GC (curve 1), VA-NCNT/GC (curve 2), and VA-NCNT (curve 3) electrodes. (c) CO-poisoning effect on *i*-t chronoamperometric response for the Pt-C/GC and VA-NCNT/GC electrodes. The arrow indicates the addition of 55 mL  $\text{min}^{-1}$  CO gas into the 550 mL  $\text{min}^{-1}$   $\text{O}_2$  flow; the mixture gas of  $\sim 9\%$  CO (volume/volume) was then introduced into the electrochemical cell. (d) Calculated charge density distribution for the NCNTs [15].

observed for commercially available Pt/C catalyst [19]. Our recent efforts [32] have successfully synthesized N-doped carbon spheres (NCS-H) by directly pyrolyzing a nebulized solution of xylene and ethylenediamine via spray pyrolysis, without using a catalyst. From the SEM image of the NCS-H in Fig. 2a, some perfect carbon spheres with a smooth surface and a narrow diameter ranging from 130 to 180 nm can be clearly observed. To investigate the electrocatalytic activity of the NCS-H, cyclic voltammograms (CVs) and linear sweep voltammetry (LSVs) were measured. Equal amounts of each catalyst were loaded on a glassy carbon (GC) electrode. The polarization curves in Fig. 2b confirms that the onset potential for NCS-H is close to that of the Pt/C catalyst, but its current density at  $-0.6$  V is higher. From Fig. 2c and d, it can be confirmed that the NCS-H has a long-term stability and excellent resistance to crossover effect compared to Pt/C catalysts. These results confirm that NCS-H holds high promise for use in methanol and alkaline fuel cells. Xia's group have also proposed a facile, catalyst-free thermal annealing approach for large scale synthesis of N-doped graphenes using low-cost industrial material melamine as the nitrogen source. Electrochemical characterization of these N-doped graphenes has clearly demonstrated their excellent electrocatalytic activity for the oxygen reduction reaction (ORR) in alkaline electrolytes [33]. Considering the above-described wholly metal-free preparation procedures for such N-doped carbon materials, their electrocatalytic activity can be attributed exclusively to the incorporation of nitrogen, and C–N structure is expected to play a decisive role in the observed ORR activity enhancement.

According to previous reports, nitrogen atoms can be substitutionally incorporated into the basal plane of graphene in the form of “pyridinic”, “pyrolic”, and “graphitic” nitrogen bonding configurations [35]. Pyridinic N refers to N atoms at the edges of graphene planes, where each N atom is bonded to two carbon atoms and donates one p-electron to the aromatic  $\pi$  system. Pyrrolic N atoms are incorporated into five member heterocyclic rings, where each N

atom is bonded to two carbon atoms and contributes two p-electrons to the  $\pi$  system. Graphitic N atoms are incorporated into the graphene layer and substitute carbon atoms within the graphene plane (Fig. 3). It is believed that nitrogen environment affects the electronic structure of doped carbon materials and results in different mechanisms of activity enhancement. Thus, it is important to clarify the correlation between nitrogen bonding configuration and ORR performance.

Graphitic N atoms have been reported both experimentally and theoretically to serve as ORR catalytic sites due to their reduced adsorption energy. Kim et al. found that graphene edge structures became more catalytically active after introduction of graphitic N. It was proposed that such structures not only enhance the first electron transfer rate, but also show preference for the in particular  $4e^-$  reduction pathway [36]. Liu's report also suggested that the significantly enhanced activity and selectivity of nitrogen-doped ordered mesoporous graphitic arrays should be attributed to the combination of the highly graphitic nature of this material and its increased proportion of graphite-like nitrogen atom mesostructures [19]. Recently, Lai et al. demonstrated successful fabrication of N-doped graphenes with well-defined N types by the annealing of graphene oxide under ammonia and by the annealing of reduced graphene oxide/N-containing polymer (polyaniline or polypyrrole) composites. It was found that the electrocatalytic activity of the N-doped graphene catalyst mainly depended on the graphitic N content, which determined the limiting current density, while the pyridinic N species may have converted the ORR reaction mechanism from a  $2e^-$  dominated process to a  $4e^-$  dominated process and improved the ORR onset potential [37]. All of the above reports indicate that graphitic N is a high activity site that accelerates ORR.

Though some progress toward the identity and role of the electrocatalytic active center has been made, the precise relationship between catalytic activity and nitrogen species, especially pyridinic and pyrrolic N, is still unclear [28]. Qu et al. synthesized N-doped

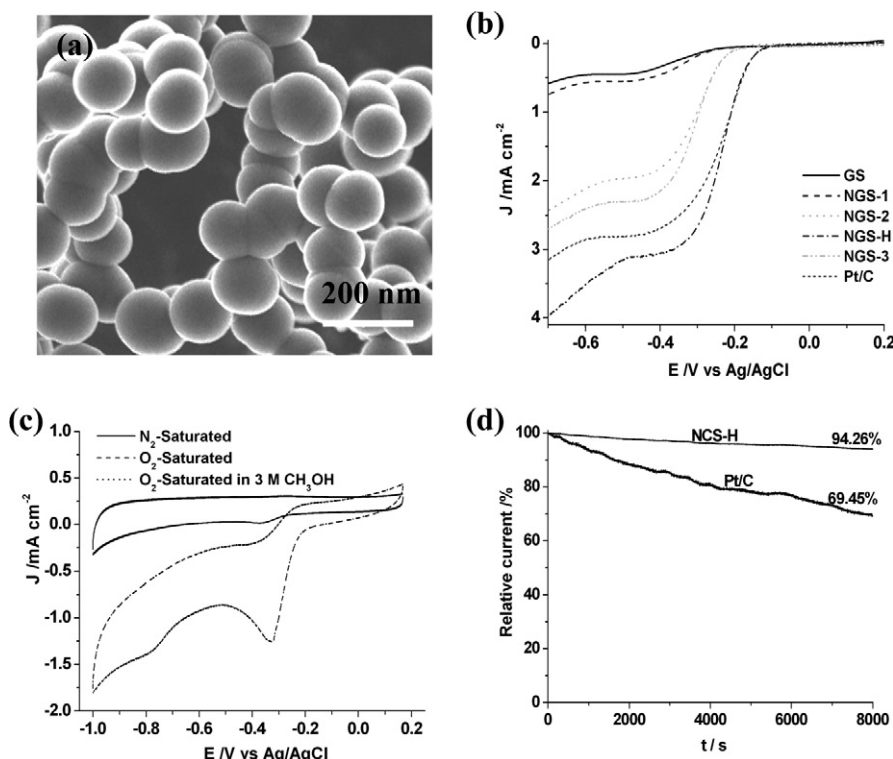


Fig. 2. (a) SEM image for NCS-H, (b) Polarization curves for various carbon spheres and a Pt/C catalyst on a glass carbon rotating disk electrode saturated in  $\text{O}_2$ , at a rotation rate of 1600 rpm, Cyclic voltammograms for (c) NCS-H and (d) the Pt/C catalyst for oxygen reduction in a 0.1 M KOH solution, saturated with  $\text{N}_2$  or  $\text{O}_2$  [32].

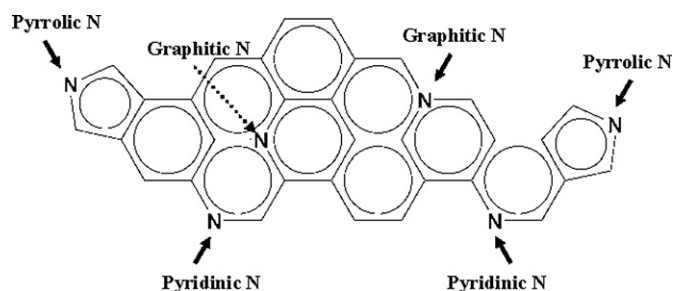


Fig. 3. Bonding configurations for nitrogen atoms in N-doped carbon materials.

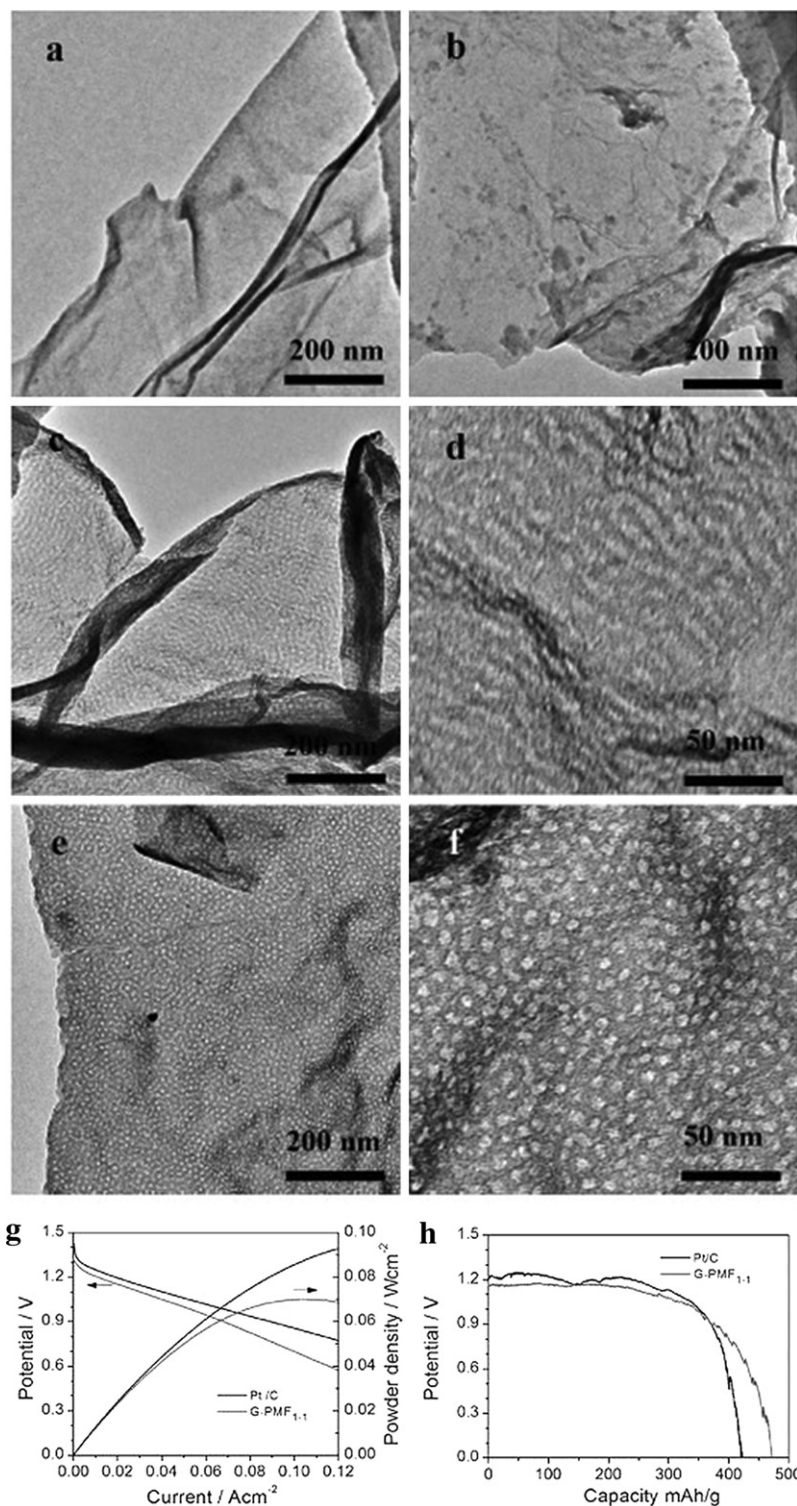
graphene with a limiting current density three times larger than that of 20 wt% Pt/C by chemical vapor deposition of methane in the presence of ammonia. It was proposed that its improved ORR activity was due to the pyridinic N-abundant structure [20]. Matter et al. also suggested that more active carbon catalysts might contain a greater amount of pyridinic nitrogen with a higher proportion of edge planes [38]. Horn, Lee, Rao and Kurak et al. also reached the same conclusion [39–42]. However, Lai et al. recently found that N-doped graphene with pyridinic-N as the dominant dopant prepared via a CVD method did not show remarkable ORR catalytic ability as previously reported [43]. Luo's report involving the synthesis of single layer graphene doped with pure pyridinic N by thermal chemical vapor deposition also confirmed that N-doped graphene only has a  $2e^-$  reduction mechanism for ORR, which suggests that pyridinic N may not be an effective promoter of ORR activity for carbon materials [44]. The above conflicting results may be attributed to the scarcity of studies in this field and variation in experimental conditions. In addition, it is also apparent that pyridinic N and pyrrolic N are always located at edge sites, as a marker of edge plane exposure. Thus, it is uncertain as to whether the pyridinic or pyrrolic N provides actual active sites for promoting ORR, or whether the reaction is simply more favorable due to an abundance of highly active edges and/or defect sites. In summary, comparison of a series of as-prepared catalysts confirms that graphitic N-dominated catalysts have higher catalytic activity with larger limiting current density than those of pyrrolic or pyridinic N-dominated catalysts. While N-doped carbon materials are promising materials for use as an ORR catalyst, deeper understanding of the relationship between N species, especially pyridinic N and pyrrolic N, and catalyst activity is still required.

Nitrogen content is also related to the ORR activity of N-graphene. Generally speaking, doped carbon materials with high nitrogen content usually provide more active reaction sites than other N-carbon materials and seem to be more feasible metal-free ORR electrocatalysts. Thus, development of a completely metal-free ORR electrocatalyst with high nitrogen content will be of scientific importance. In the past few years, some hydrocarbons with high N contents such as ethylenediamine, triazines, urea, and especially melamines, have become remarkable materials for the fabrication of N-doped carbon nanomaterials with graphitic structures [45–48]. For example, Yang et al. demonstrated successful fabrication of graphene-based carbon nitride (G-CN) nanosheets by employing graphene-based mesoporous silica nanosheets as a template and ethylenediamine and carbon tetrachloride as CN precursors. Elemental analysis revealed that nitrogen content of the resulting G-CN composite reached 19 wt% [48]. Wang et al. reported that carbon nanotubes with N-doping levels as high as 20 atom% can be directly synthesized using melamine as the C/N precursor by detonation-assisted chemical vapor deposition in a sealed vessel [49]. Han's group synthesized N-doped porous graphitic carbons (NPGCs) with hierarchical nanopores containing as high as

20.9 wt% nitrogen using cheap nano- $\text{CaCO}_3$  as template, melamine-formaldehyde resin as carbon precursor, and dilute HCl as template removing agent [50]. Furthermore, graphitic-carbon nitride ( $\text{C}_3\text{N}_4$ ) has also generated tremendous interest recently among material researchers because of its high nitrogen content and facile synthesis procedure. Zheng et al. synthesized nanoporous g- $\text{C}_3\text{N}_4$ @CMK-3 catalyst by mesoporous carbon (CMK-3) as a conductive support. The resulting catalyst exhibited a much higher ORR activity than that of pure g- $\text{C}_3\text{N}_4$ , which is also competitive in relation to a commercial Pt/C catalyst [51]. Shi et al. also immobilized g- $\text{C}_3\text{N}_4$  onto graphene sheets to form g- $\text{C}_3\text{N}_4$ /graphene composites in a liquid-phase solution. These composites exhibited enhanced electrocatalytic activity for ORR and CO tolerance comparable to that of 23 wt% Pt nanoparticles supported on graphene sheets [52].

Because N-doped carbon materials usually consist of macroscopic and microscopic structures and the content of different nitrogen types usually varies with nitrogen doping level, a higher amount of N incorporated in the carbon host alone does not always lead to better performance, which also crucially depends on structural and morphological properties [38]. Recently, different studies have produced contradictory results. Control of macroscopic and microscopic structure in N-doped carbon materials is therefore also an important research topic. Development of N-doped carbon materials with high surface area and a well-defined porous structure which facilitates reactant transport is a potential solution to obtain ideal NPMCs with more realistic value for fuel cell applications. Yang et al. prepared mesoporous nitrogen-doped carbon materials with high surface areas of up to  $1500 \text{ m}^2 \text{ g}^{-1}$  by the carbonization of nucleobases dissolved in an all-organic ionic liquid via hard templating with silica nanoparticles. It was demonstrated that the resulting nitrogen-doped carbons had very high catalytic activity for the ORR for fuel cells, even in the metal-free case. Specifically, the as-prepared materials exhibited a low onset voltage for ORR in alkaline medium and high methanol tolerance compared with those of commercial 20 wt% Pt/C catalyst [21]. Shi's group [53] reported a simple and effective method to develop and fabricate nanoporous N-doped carbon modified graphene using Pluronic F127 [(polyethyleneoxide)<sub>99</sub>-(polypropyleneoxide)<sub>67</sub>-(polyethyleneoxide)<sub>99</sub>] as a soft template. Fig. 4 shows the TEM images of the resulting graphene based composite sheets (G-PMFs) obtained at different volume ratios of reduced graphene oxide (RGO) and phenol-melamine-formaldehyde (PMF). The G-PMFs had a sandwich structure with one graphene layer and two nanoporous nitrogen-doped carbon layers. The electrocatalytic results demonstrate that the G-PMFs have high electrocatalytic activity, good durability, and high selectivity for the ORR. To further evaluate the performances of the G-PMF catalysts in real FCs, the Zn-air batteries by using GPMF<sub>1-1</sub> as the air electrodes were fabricated. The open circuit voltage of this battery is about 1.3 V (Fig. 4g), and this value is about 0.1 V lower than that of the battery with a Pt/C anode (1.4 V). Discharge tests were also carried out to examine the real performances of the Zn-air batteries in the working status (Fig. 4h). In this case, the discharge voltage of the Zn-air battery based on G-MPF<sub>1-1</sub> was found to be about 1.15 V, which is slightly lower than the voltage of the battery based on the Pt/C anode. The capacity of the G-MPF<sub>1-1</sub>-based battery was measured to be as high as  $400 \text{ mA h g}^{-1}$  by discharging to a cut off voltage of 0.9 V, which is nearly the same as that of the battery based on the Pt/C anode. This result reflects that G-PMF is promising for replacing traditional Pt/C in Zn-air batteries. Furthermore, Liang et al. successfully designed and constructed a three-dimensionally ordered macroporous g- $\text{C}_3\text{N}_4$ /C catalyst using silica microspheres as hard templates. This novel catalyst possessed a prominent ORR catalytic activity comparable with commercial Pt/C





**Fig. 4.** TEM images of (a) graphene, (b) G-PMF<sub>2-1</sub>, (c and d) G-PMF<sub>1-1</sub> and (e and f) G-PMF<sub>1-3</sub>. (g) Polarization curves of the Zn–air battery with a G-PMF<sub>1-1</sub> or Pt/C anode. (h) Discharge curve of the Zn–air battery with a G-PMF<sub>1-1</sub> or Pt/C air electrode at a discharging current density of 20 mA cm<sup>-2</sup> [53].

in both reaction current density and onset potential. As a metal-free catalyst, macroporous g-C<sub>3</sub>N<sub>4</sub>/C also showed much better fuel crossover resistance and long-term durability than commercial Pt/C in alkaline medium [54]. The development of doped carbon catalysts with 3D macroporous structure may be an important research strategy to obtain ideal NPMCs with realistic value for fuel cell applications.

## 2.2. Other heteroatom (B, P, S and Se) doped carbon nanomaterials as ORR catalysts

Recently, research involving the electrocatalytic activities of carbon materials doped with other low (e.g. B, P) or similarly (e.g. S, Se) electronegative atoms have attracted increasing attention [24]. Hu et al. demonstrated the successful fabrication of B-doped carbon

nanotubes (BCNTs) by chemical vapor deposition with benzene, triphenylborane, and ferrocene as precursors and catalyst. They found that the resulting BCNTs exhibited good performance for the ORR in terms of electrocatalytic activity, stability, and immunity toward ethanol crossover and CO poisoning. Electrocatalytic performance improved progressively with increasing boron content, as reflected by an increased reduction current and positively shifted onset and peak potentials. Subsequently, Sheng's report [55] also confirmed that B doping improves the electrocatalytic performance of graphene. Theoretical calculations have proven that the electrocatalytic ability of BCNTs for ORR stems from electron accumulation in the vacant  $2p_z$  orbital of boron dopant from the  $\pi^*$  electrons of the conjugated system; transfer then readily occurs to the chemisorbed  $O_2$  molecules with boron as a bridge. The transferred charge weakens the O–O bonds and facilitates the ORR on the BCNTs. Furthermore, Hu also proposed that breaking the electroneutrality of graphitic materials to create charged sites favorable for  $O_2$  adsorption is a key factor in enhancing ORR activity, regardless of whether the dopants are N or B atoms. This view also suggests that tailoring of the electronic arrangement of graphite materials by doping could be a practical strategy for producing significantly improved materials for ORRs in FC.

Phosphorus, as one of the nitrogen group elements, has the same number of valence electrons as nitrogen and often shows similar chemical properties. Recently, Peng's group prepared a P-doped graphite layer catalyst without any metal residue that exhibited high electrocatalytic activity, long-term stability, and excellent tolerance to methanol cross-over effects for the oxygen reduction reaction in an alkaline medium [23]. Subsequently, phosphorus-doped multiwalled carbon nanotubes were also reported to show much higher ORR activity than commercial Pt/C in alkaline fuel cells [56].

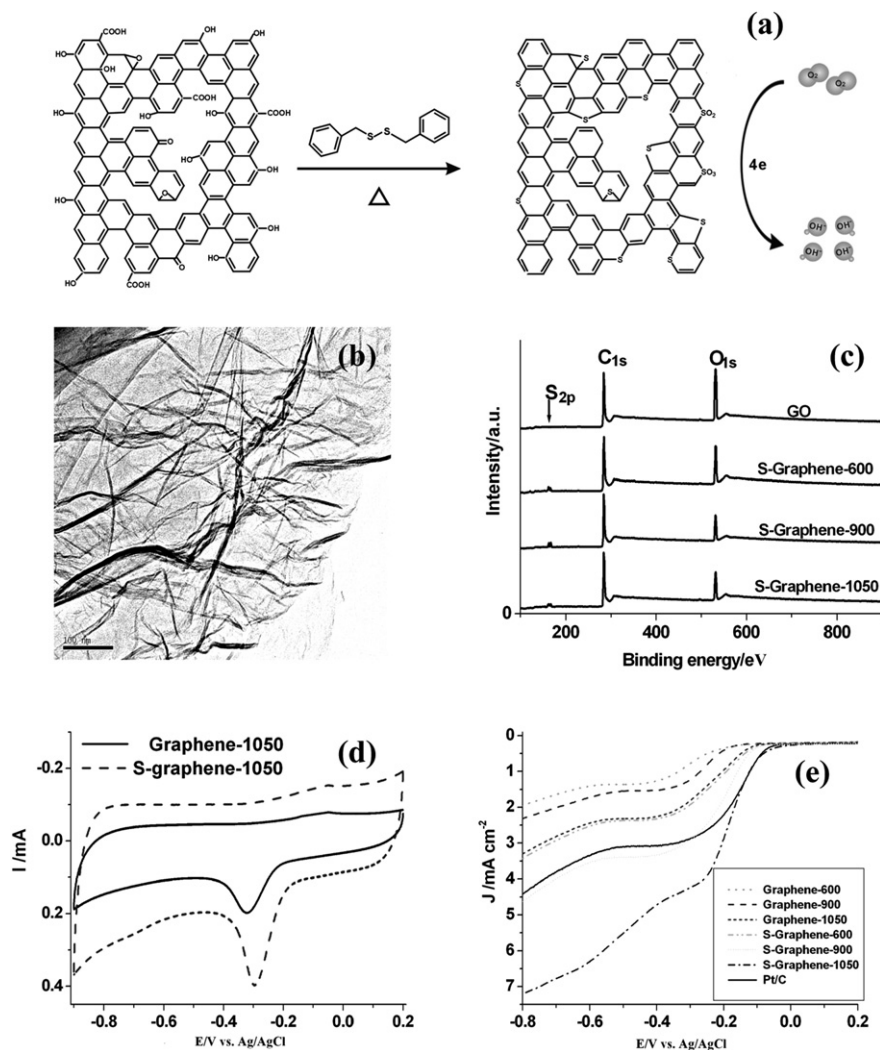
After carbon materials doped with atoms having larger (N) or smaller (P, B) electronegativity than carbon had been confirmed to improve the electrocatalytic performance of graphene, interest turned to the development of carbon materials doped with elements of similar electronegativity to carbon. Sulfur (electronegativity: 2.58) has an electronegativity close to that of carbon (2.55). Our recent efforts [25] have resulted in successful fabrication of sulfur-doped graphene (S-graphene) by direct annealing of graphene oxide (GO) and benzyl disulfide (BDS) in argon (Fig. 5). The resulting electrocatalytic performances indicated that the S-graphenes can exhibit excellent catalytic activity, long-term stability, and high methanol tolerance in alkaline media for ORRs (Fig. 5c). Moreover, we also found that the graphenes doped with other elements of similar electronegativity to carbon such as selenium (electronegativity: 2.55) show similarly high ORR catalytic activity [26]. Very recently, Yang et al. also confirmed that S-doped graphene synthesized via thermal reaction between graphene oxide and  $H_2S$  gas can act as a metal-free electrocatalyst for oxygen reduction reactions, showing comparable electrocatalytic activity to that of commercially available Pt/C [57]. According to previous reports [24] involving the origin of this ORR activity enhancement with the N (or B) doped carbon materials, breaking the electroneutrality of graphitic materials would create favorable positive charged sites for the side-on  $O_2$  surface adsorption. This parallel diatomic adsorption could effectively weaken the O–O bonding and facilitate the direct reduction of oxygen to  $OH^-$ . However, in these above cases, unlike nitrogen (or boron) dopant, sulfur (or Se) has a close electroneutrality to carbon. Obviously, the previous views cannot explain the observations herein. It is proposed that breaking the electroneutrality of graphitic materials may not be necessary factor for the ORR activity enhancement, while the unique electron structure derived from the conjugation between the sulfur lone-pair electrons and the graphene  $\pi$  system may play

a vital role for the high ORR activity of S-graphene. According to this new understanding, it is suggested that tailoring the  $\pi$  electronic system of graphene may be a preferred factor for producing significantly improved materials for ORRs, regardless of any dopants. Thus, it is believed that other dopants, which can effectively tailor the  $\pi$  system of graphene, may also enhance the ORR catalytic activity. These new types of heterodoped structures may provide opportunities for further developing low-cost NPMCs with high activities and long lifetimes for practical FC applications.

### 2.3. Dual or treble doped carbon nanomaterials as ORR catalysts

After single heteroatom doping had been confirmed to improve the electrocatalytic performance of carbon materials, development of carbon materials doped with dual or multi heteroatoms motivated our curiosity. Recently, Wang et al. prepared vertically aligned B and N co-doped carbon nanotubes (VA-BCN) by pyrolysis of melamine diborate, a single-compound source of carbon, boron, and nitrogen for VA-BCN growth. The resultant VA-BCN electrode exhibited higher electrocatalytic activity for ORR in alkaline medium than its counterparts doped with boron or nitrogen alone [58]. Wang proposed that the improved activity was likely due to a synergetic effect arising from co-doping of the CNTs with boron and nitrogen. Subsequently, metal free B and N co-doped graphene (BCN graphene) was also developed, by thermal annealing GO in the presence of boric acid and ammonia [59]. From Fig. 6b, it is interesting to see that the half-wave potential of the  $B_{12}C_{77}N_{11}$  (with a modest N- and B-doping level) electrode for ORR in 0.1 M KOH solution was at around  $-0.25$  V, which is close to that of the Pt/C but much more positive than those of other BCN graphene electrodes. Furthermore, the current density of ORR on  $B_{12}C_{77}N_{11}$  within almost the whole potential range covered in this study is higher than that of the other BCN and Pt/C electrodes. The current–time ( $i-t$ ) chronoamperometric responses for ORR at the BCN graphene ( $B_{12}C_{77}N_{11}$ ) and Pt/C electrodes are given in Fig. 6c. For the Pt/C electrode, a sharp decrease in current upon the addition of 3.0 M methanol can be observed. In contrast, the amperometric response from the BCN graphene electrode remained almost unchanged even after the addition of methanol. Fig. 6c shows the durability test for the BCN graphene electrode. As can be seen, the continuous oxygen reduction reaction (ca. 40,000 s) at  $-0.2$  V (vs. SCE) caused only a slight loss (10%) of the current density before leveling off. In contrast, the corresponding current loss on Pt/C electrode under the same condition was as high as about 55%. All the results also suggest that the B and N co-doped graphene can act as an efficient low-cost metal-free ORR electrocatalyst for FCs and other applications.

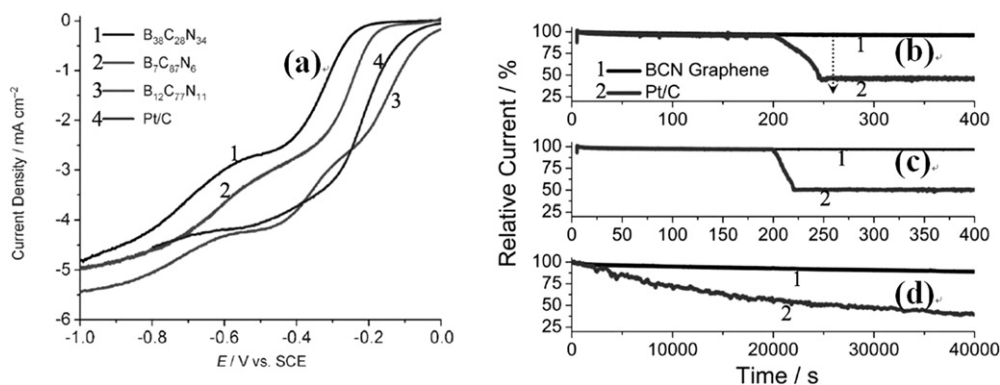
Additional doping of P (or S) into N-doped carbon is also an effective strategy for developing the enhanced ORR activity. Choi et al. reported P, N-doped carbon prepared via pyrolysis of DCDA and phosphoric acid, as sources of C–N and P, respectively, onto  $CoCl_2$  and  $FeCl_2$ . It was confirmed that additional P-doping promotes the catalytic activity of NDC, and an optimized PNDC exhibited a more than four-fold increase in ORR mass activity compared with that of NDC [60]. Nitrogen and sulfur co-doped carbon materials were synthesized via pyrolysis of composites composed of iron chloride, cobalt chloride, and five different amino acids (alanine, cysteine, glycine, niacine, and valine), and their electrocatalytic activity toward oxygen reduction reactions (ORR) for fuel cell applications compared. Among all the catalysts obtained, the dual-doped carbon catalysts showed the highest onset potential and electrochemical activity in acidic media, about 43% of that of commercial Pt/C (40 wt%). It was surmised that not only nitrogen doping but also sulfur doping of carbon plays a key role in improving electrocatalytic activity of ORR [61]. Wohlgemuth et al.



**Fig. 5.** (a) Schematic illustration of S-graphene preparation, (b) TEM, image of S-graphene-1050, (c) XPS spectra of GO, S-graphene-600, S-graphene-900 and S-graphene-1050, (d) Cyclic voltammograms for Graphene-1050 and S-graphene-1050, (e) LSV curves for various graphenes and a Pt/C catalyst on a glass carbon rotating disk electrode saturated in  $O_2$  at a rotation rate of 1600 rpm [25].

reported a simple, metal-free route toward nitrogen- and sulfur-doped, high surface area carbon aerogels based on our previously reported glucose–ovalbumin system. By comparing solely nitrogen-doped with nitrogen- and sulfur-doped carbon aerogels, it

was observed that the presence of sulfur improved the overall electrocatalytic activity of the carbon material in both basic and acidic media [62]. This study of the synergistic effect of combined sulfur (or phosphorus or boron) and nitrogen-doping in catalysis of



**Fig. 6.** (a) LSV curves of ORR on BCN graphene with different compositions in oxygen-saturated 0.1 M KOH solution at  $10 \text{ mV s}^{-1}$  and compared with the commercial Pt/C electrocatalyst. The  $i-t$  curves of ORR at  $-0.2 \text{ V vs. SCE}$  on graphene ( $B_{12}C_{77}N_{11}$ , black) and Pt/C (red) electrodes in oxygen saturated 0.1 M KOH solutions with the rotation rate of 1000 rpm (b) 3.0 M methanol was added at around 200 s; (c) CO was introduced at around 200 s; (d) durability testing for 40,000 s [59]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



the “oxygen reduction reaction” (ORR) is expected to be significant to future research in improvement of heterogenous, metal-free, carbon-based catalysts.

The first ternary (N, B, P)-doped carbon to be adapted as an ORR catalyst was very recently reported [63], and further demonstrated that additional B and/or P doping modifies carbon characteristics and improves the ORR activity of N-doped carbon catalysts. It has been proposed that B-doping may increase the portion of pyridinic-N sites for various types of N-doping and magnifies the amount of  $sp^2$ -carbon structures, while P-doping enhances the charge delocalization of the carbon atoms and constructs a morphology with many open edge sites that are split and wrinkled. These results imply that binary or ternary doping of B and P with N into carbon induces remarkable performance enhancements, and that charge delocalization of the carbon atoms and number of edge sites are significant factors in deciding oxygen reduction activity in carbon-based catalysts.

#### 2.4. Surface transfer doped carbon nanomaterials as ORR catalysts

From a large amount of literature, doping of graphite materials may be briefly classified as substitutional doping or surface transfer doping. Substitutional doping refers to the substitution of carbon atoms in the honeycomb lattice of graphene sheet by atoms with a different number of valence electrons, such as nitrogen and boron. In surface transfer doping, doping is achieved by electron exchange between a semiconductor and dopants which adsorb on the surface of the semiconductor. Consequently, surface transfer doping is also called adsorbate-induced doping. According to Hu's theoretical studies [24], breaking the electroneutrality of graphitic materials to create charged sites favorable for  $O_2$  adsorption is a key factor in enhancing ORR activity, regardless of whether the dopants are N or B atoms. Obviously, tailoring the electronic arrangement of graphene (or CNTs) by doping could be a practical strategy for producing significantly improved materials for ORRs in FC. Generally speaking, adsorption of molecules with electron withdrawing groups to the surface of graphene will lead to p-type doping, and molecules with donating groups will lead to n-type doping. Recently, Dai and co-workers [64,65] have demonstrated that poly(diallyldimethylammonium chloride) (PDDA), which has a strong electron-withdrawing ability, is able to adsorb on pure carbon CNTs (or graphene). It is notable that the adsorbed-PDDA CNT (or graphene) electrode possessed remarkable electrocatalytic properties for ORR, similar to that of commercially available Pt/C electrode but with better fuel selectivity and long-term durability.

Our groups [66] have developed a  $MnO_x$ -CNT (Fig. 7) ORR catalyst ( $\sim 0.85$  wt%  $MnO_x$ ), fabricated through a simple electrochemical deposition method. As shown in Fig. 7d and e, the CV curve for  $MnO_x$ -CNT electrode in  $O_2$  shows a distinct peak at  $-0.35$  V, which corresponds to the  $O_2$  reduction reaction. The reduction current ( $542 \mu A$ ) is more than four times larger than that of the commercial Pt/C catalyst ( $135 \mu A$ ). The result suggests that  $MnO_x$ -CNTs have more pronounced catalytic activity for ORR than the commercial Pt/C catalyst. Moreover, compared with the catalytic performance of  $MnO_x$  on other substrates ( $MnO_x$ -CB,  $MnO_x$ -KS-6), the  $MnO_x$ -CNTs exhibit remarkably higher catalytic activity (Fig. 7e). Our results also suggest the irreplaceable role of CNTs for excellent ORR activity. Considering the very low  $MnO_x$  content (only 0.85 wt%) and low catalytic activity of other  $MnO_x$  samples on different substrates, we speculate that the catalytic activity originating from  $MnO_x$  in the  $MnO_x$ -CNTs may be limited. After analyzing the electronic structure of the  $MnO_x$ -CNT surface through XPS (Fig. 7f and g), we found that electron transfer occurs from the CNTs to the Mn ions and that a high positive charge is

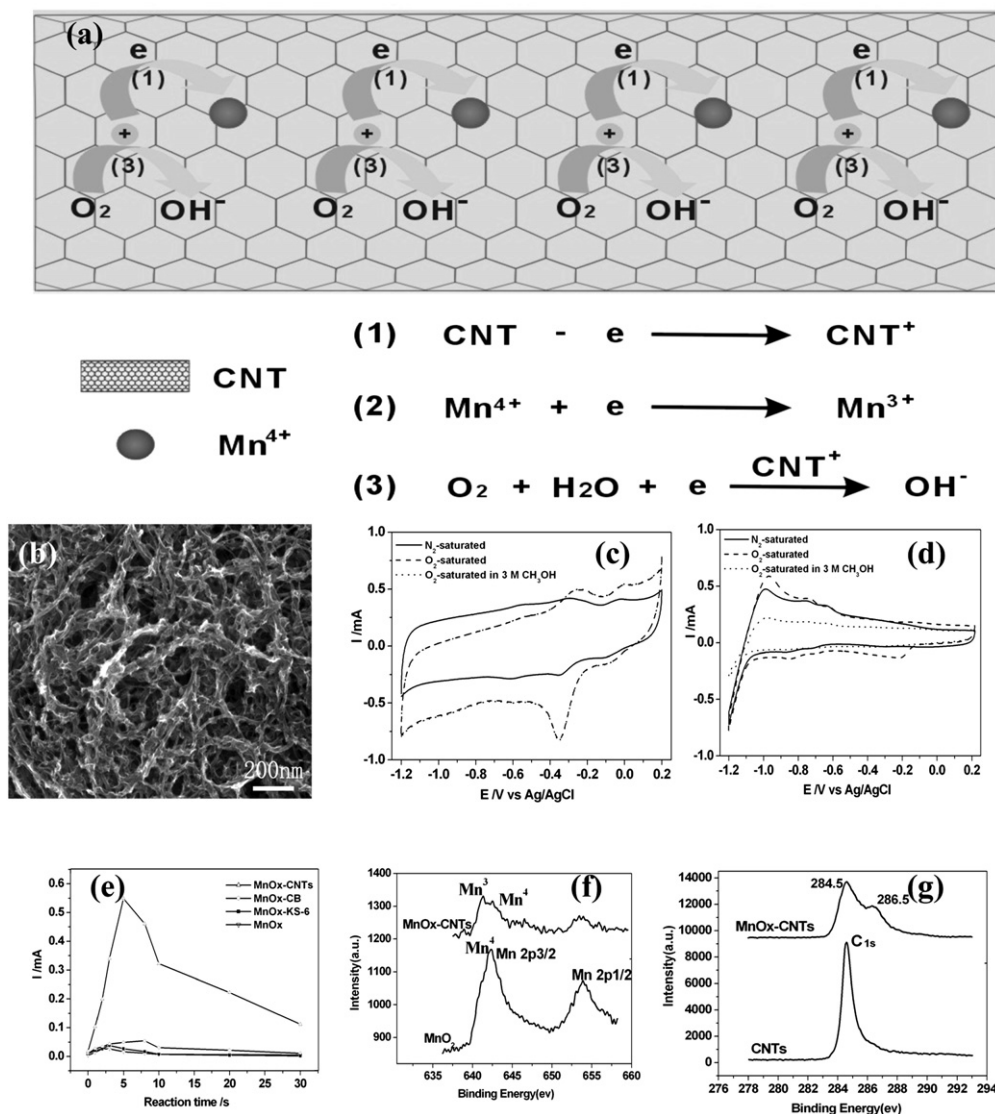
generated on CNT surface (Fig. 7a). The electronic structure characteristics of these high-activity  $MnO_x$ -CNTs are very similar to the structural model of N-doped CNTs proposed by Dai [15] and Hu [24]. The high positive charge on the CNT surface is believed to be the origin of the catalytic activity observed for  $MnO_x$ -CNTs in the ORR.

Very recently, we also reported the successful fabrication of I-doped graphene (Fig. 8) by direct annealing of graphene oxide (GO) and iodine in argon [27]. Raman spectroscopy and XPS results confirmed that polyiodides appeared on the resulting graphene and that electron transfer between atomic iodine and the graphene surface resulted in the presence of polyiodides with negative charge ( $I^{3-}$  and  $I^{5-}$ ) and graphene with positive charge (Fig. 8c). As expected, the positive charge was very favorable for adsorbing  $O_2$  onto the graphene surface of and thereby promoting ORR. These I-graphenes exhibited excellent catalytic activity, long-term stability, and high methanol tolerance in alkaline media for ORRs (Fig. 8d and e). These results clearly indicate that the important role of intermolecular charge-transfer to ORR is applicable to carbon nanomaterials in general for the development of various other metal-free efficient ORR catalysts for fuel cell applications.

#### 2.5. Composites based on heteroatom doped carbon nanomaterials as ORR electrocatalysts

Carbon nanomaterials, including one-dimensional (1D) CNTs and two-dimensional (2D) graphene, have been widely applied in electrochemical fields due to their superior electrical conductivity, large surface area, and high chemical stability. Nitrogen-doped carbon nanomaterials with better conductivity compared with undoped ones have also been used as catalyst supports in fuel cells. The presence of the nitrogen species results in good coverage and dispersion of the in situ synthesized Pt NPs compared with the undoped graphene surface. This advantage, along with the N-doping induced increase of the electronic conductivity, has led to much enhanced electrocatalytic activities for carbon nanomaterials. Hu et al. [67] developed a facile strategy for the construction of Pt–Co/ $CN_x$  electrocatalysts in which Pt-based alloyed nanoparticles with a size of about 3 nm were highly and homogeneously dispersed on  $CN_x$  nanotubes (Fig. 9). Compared with commercial Pt/C and monometallic Pt/ $CN_x$  catalysts, these binary Pt–Co/ $CN_x$  catalysts showed much higher electrocatalytic activities and similar stabilities for oxygen reduction in acidic electrolyte, but with far lower consumption of expensive Pt (Fig. 9j and k). It was proposed that the good performance of the catalysts mainly arose from the i) high dispersion of Pt-based species, ii) alloying effect of Pt/Co, and iii) intrinsic catalytic capacity of the highly conductive  $CN_x$  nanotubes. These results indicate that strategic design of an electrocatalyst by immobilizing Pt-based alloyed nanoparticles onto  $CN_x$  nanotubes is quite promising for ORR catalysis in PEMFC. Sun et al. synthesized ultrathin single crystal platinum nanowires with diameters of  $\sim 2.5$  nm and lengths of up to 100 nm on nitrogen-doped CNTs (N-CNTs) via a straightforward wet chemical method in an environmentally friendly aqueous solution at room temperature, without any stabilizing agent. These ultrathin nanowires and their N-CNT composites hold potential for a wide range of applications. It is believed that widely distributed defects on the N-CNTs surface, associated with N incorporation, confine the Pt atoms and play a key role in the formation of tiny nuclei that further leads to anisotropic growth of ultrathin nanowires [68]. Chen et al. synthesized CNTs and  $CN_x$  with a floating chemical vapor deposition method under similar conditions for a comparative test. Pt nanoparticles were deposited on these two supports with an ethylene glycol reduction method. Pt/ $CN_x$  showed a more uniform dispersion with smaller particle size than Pt/CNTs and exhibited a higher



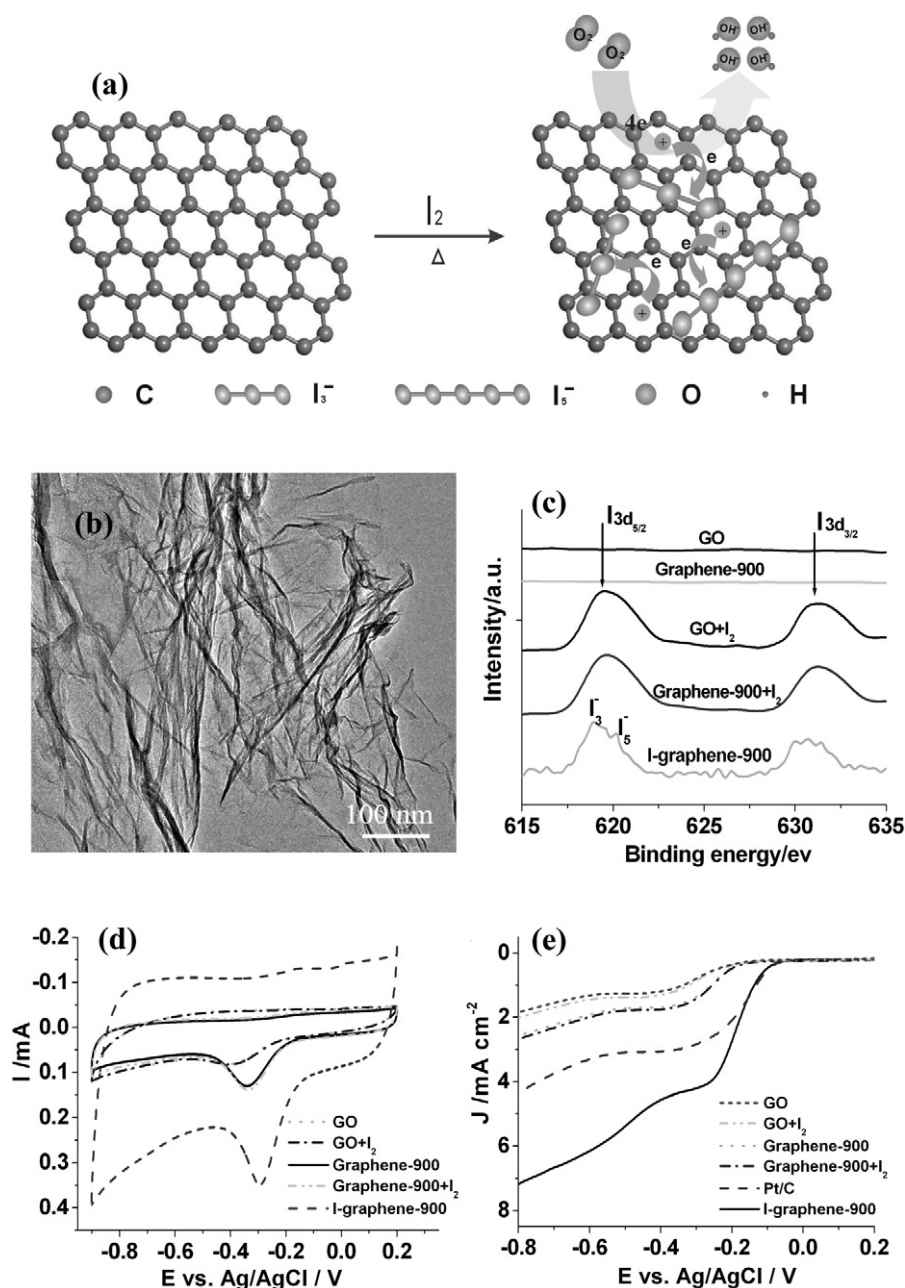


**Fig. 7.** (a) Schematic diagram for the MnO<sub>x</sub>-CNT ORR mechanism, (b) SEM image of the MnO<sub>x</sub>-CNT, cyclic voltammograms of (c) MnO<sub>x</sub>-CNTs and (d) the commercial Pt/C catalyst for oxygen reduction in 0.1 M KOH solution saturated with N<sub>2</sub> or O<sub>2</sub>, (e) the reduction current versus reaction time for four MnO<sub>x</sub> on different substrate, XPS spectra high-resolution (f, upper) Mn<sub>2p</sub> and (g, upper) C<sub>1s</sub> for the Mn-doped CNTs, (f, bottom) Mn<sub>2p</sub> of MnO<sub>2</sub> and (g, bottom) C<sub>1s</sub> of pristine CNTs [66].

catalytic activity for ORR, as indicated by a larger kinetic current, higher half-wave potential, and higher four-electron transfer efficiency to H<sub>2</sub>O. Pt/CN<sub>x</sub> also showed higher fuel cell performance as a cathode catalyst in a single cell test than Pt/CNTs [69].

Non-precious metal catalysts supported on N-graphene have also been studied for ORR. Wen et al. reported a synthetic strategy that enables facile, economical, and scalable synthesis of nitrogen-enriched core-shell structured catalysts with iron-based composite (Fe/Fe<sub>3</sub>C) nanorods as the core and graphite carbon as the shell (N-Fe/Fe<sub>3</sub>C@C) [70]. N-Fe/Fe<sub>3</sub>C@C showed significantly improved activities and advanced kinetics for ORR in neutral phosphate buffer solution (PBS) compared with commercial Pt/C catalysts (10% Pt). A comprehensive comparison was conducted between N-Fe/Fe<sub>3</sub>C@C and Pt/C cathode catalysts for microbial fuel cells (MFC), showing that N-Fe/Fe<sub>3</sub>C@C-MFC predominately excelled over Pt/C-MFC in terms of power density and coulombic efficiency. Because the N-Fe/Fe<sub>3</sub>C@C catalyst also works efficiently in alkaline and acid solutions, it offers an alternative cathode material suitable for various fuel cells and metal-air batteries. Wu et al. successfully

fabricated three-dimensional N-doped graphene aerogel-supported Fe<sub>3</sub>O<sub>4</sub> nanoparticles via a combined hydrothermal self-assembly, freeze-drying, and thermal treatment process. Because of their 3D macroporous structure and high surface area, the resulting Fe<sub>3</sub>O<sub>4</sub>/N-GAs show excellent electrocatalytic activity for the ORR in alkaline electrolytes, exhibiting higher current density, lower ring current, lower H<sub>2</sub>O<sub>2</sub> yield, higher electron transfer number (~4), and better durability, potentially making Fe<sub>3</sub>O<sub>4</sub>/N-GAs a nonprecious metal cathode catalyst candidate for fuel cells [71]. Liang et al. [72] grew Co<sub>3</sub>O<sub>4</sub> on mildly oxidized graphene oxide (rmGO) both with and without the presence of NH<sub>4</sub>OH, obtaining Co<sub>3</sub>O<sub>4</sub>/rmGO and Co<sub>3</sub>O<sub>4</sub>/N-rmGO catalysts. It has been revealed that Co<sub>3</sub>O<sub>4</sub>/rmGO and Co<sub>3</sub>O<sub>4</sub>/N-rmGO catalysts exhibit high ORR activity that is different from that observed for Co<sub>3</sub>O<sub>4</sub> nanocrystals. The two catalysts showed an obvious four-electron ORR pathway, different to the two-electron ORR pathway of N-rmGO, also obtained in the study. Comparing their kinetic currents, Co<sub>3</sub>O<sub>4</sub>/N-rmGO exhibited higher apparent current density than Co<sub>3</sub>O<sub>4</sub>/rmGO. The higher ORR activity of Co<sub>3</sub>O<sub>4</sub>/N-rmGO was ascribed to



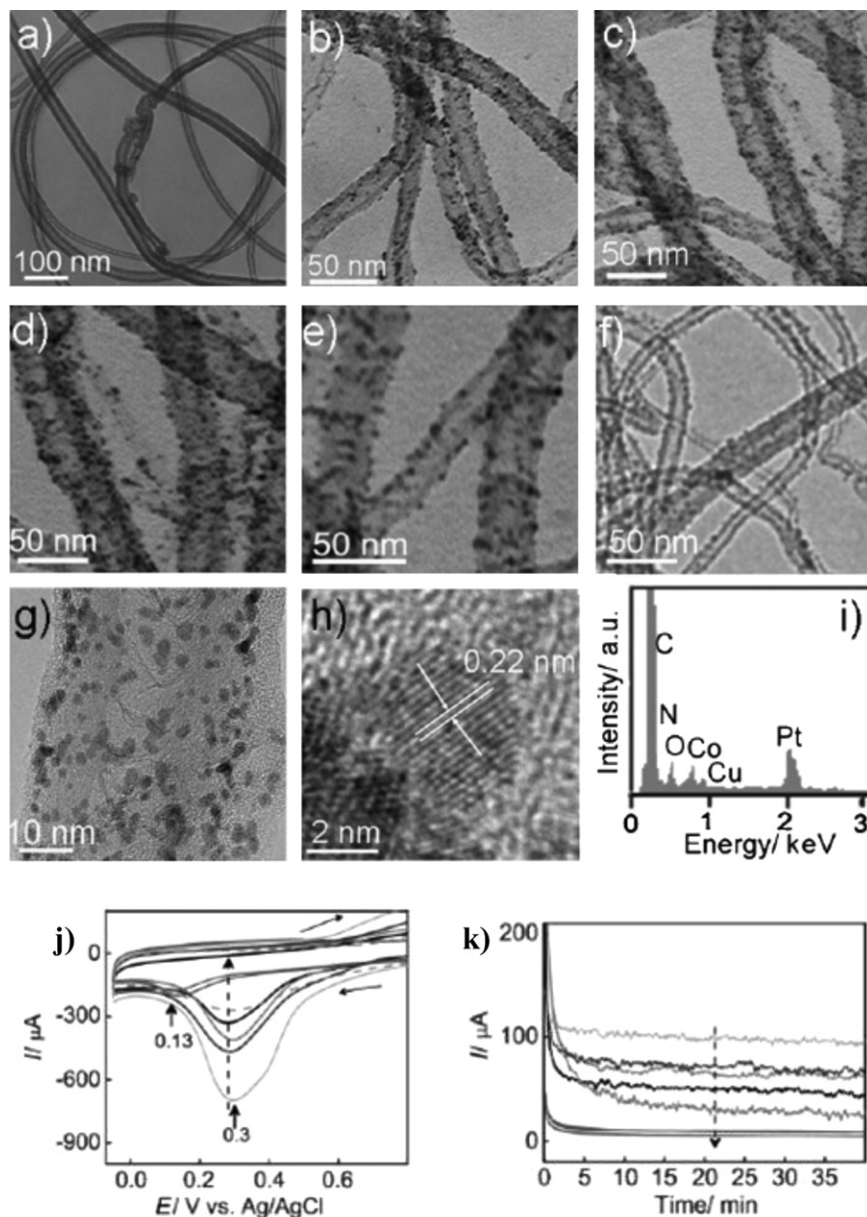
**Fig. 8.** (a) Schematic illustration of I-graphene preparation, (b) TEM images of I-graphene-900, (c) high-resolution  $I_{3d}$  spectra of GO, Graphene-900,  $GO + I_2$ , Graphene-900 +  $I_2$  and I-graphene-900, (d) Cyclic voltammograms for various graphenes, (e) LSV curves for various graphenes and a Pt/C catalyst on a glass carbon rotating disk electrode saturated in  $O_2$ , at a rotation rate of 1600 rpm [27].

synergistic coupling between  $Co_3O_4$  and N-graphene. Because  $Co_3O_4/NrnmGO$  shows both a high ORR activity similar to that of Pt catalysts and excellent stability, this kind of hybrid catalyst is also promising for ORR catalysis. Tan et al. synthesized a novel  $MnO-m-N-C$  nanocomposite via an in situ  $MnO_x$ -template method. Throughout this synthesis process and electrocatalysis, manganese oxides played very important roles, including serving as a template for carbon coating and synergetic active sites for ORR. Due to the synergetic effects between  $MnO$  and  $m-N-C$ , the resulting  $MnO-m-C$  composite catalyst exhibited high ORR activity in alkaline solution. The high surface area of the  $MnO-m-N-C$  nanocomposite, resulting from its mesoporous structure, also made a remarkable contribution to the high ORR activity observed. In addition to excellent electrocatalytic activity, the as prepared  $MnO-m-C$  composite catalyst exhibited superior stability and methanol tolerance

to commercial Pt/C catalyst for ORR, indicating a promising cathode catalyst candidate for alkaline methanol fuel cell applications [73]. The novel synthesis method described here may be extended to the preparation of many other kinds of mesoporous carbons or metal oxides-containing mesoporous carbons for wide applications including energy storage, catalysis, and electrocatalysis.

### 3. Problems and prospects

Although much effort has been made to develop new catalysts for ORR, the present metal free carbon catalysts are still far from satisfactory for large-scale practical applications. Much further research is needed to produce commercially valid NPMCs with high activity and practical durability for ORRs, which may be a



**Fig. 9.** TEM images and EDS spectrum of the catalysts. (a) CN<sub>x</sub> nanotubes, (b) Pt/CN<sub>x</sub>, (c) Pt<sub>3</sub>Co/CN<sub>x</sub>, (d) Pt<sub>3</sub>Co<sub>2</sub>/CN<sub>x</sub>, (e) PtCo/CN<sub>x</sub>, and (f) Co/CN<sub>x</sub>. (g–h) HRTEM images and (i) EDS spectrum of Pt<sub>3</sub>Co/CN<sub>x</sub>. (j) CVs of the electrocatalysts in O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>. (k) Steady-state chronoamperometry at 0.2 V with oxygen bubbling. Along arrows: Pt<sub>3</sub>Co/CN<sub>x</sub>, Pt<sub>3</sub>Co<sub>2</sub>/CN<sub>x</sub>, PtCo/CN<sub>x</sub>, Pt/CN<sub>x</sub>, Pt/C, CN<sub>x</sub> nanotubes, and Co/CN<sub>x</sub> [67].

significant topic of research trends in the future. Some problems and prospects are discussed in the literature.

- (1) The development of new low-cost carbon-based catalysts via facile, green, and cost-effective methods is still a significant issue. Although some catalysts have recently been prepared by nanocasting, chemical vapor deposition, and hard template approaches, these synthesis methods usually involve either low efficiency or laborious procedures. Thus a sample, highly effective and easily scaled-up method of developing new nanocarbon catalysts will be a viable solution to achieve the practical application of NPMs in fuel cell.
- (2) For N-doped carbon catalysts, some investigation has been carried out to clarify the correlation between nitrogen bonding configurations and ORR performance, however, the precise relationship between catalytic activity and nitrogen species is still unclear. Furthermore, it is still difficult to develop the

N-doped carbon catalysts with well-defined nitrogen species. Deeper study is thus required.

- (3) Most recent studies of ORR by heteroatom-doped carbon nanostructures focus on alkaline electrolytes, however, the activities and stabilities of these catalysts in acidic media are still insufficient. It is worth noting that most fuel cells usually operate in acidic electrolytes (particularly the proton exchange membrane fuel cell (PEMFC)). In this sense, it is expected that development of novel doped carbon catalysts with excellent performance in acidic environments will have great impact on the development of PEMFC in the coming years.
- (4) Although some recent reports have focused on research involving the origin of ORR activity enhancement for heteroatom-doped carbon nanostructures, the mechanism of activity enhancement is still unclear. According to Hu's proposal, breaking of the electroneutrality of graphitic materials by the different electroneutrality between carbon and the



dopant creates positive charged sites favorable for side-on O<sub>2</sub> surface adsorption [24]. Very recently, Zhang et al. reported that the spin density is likely more important than atomic charge density in determining the catalytic active sites, from density functional theory calculations [74]. In our case (S-doped graphene) [25], it is suggested that tailoring the  $\pi$  electronic system of graphene may be a preferred factor for producing significantly improved materials for ORRs, regardless of any dopants. Furthermore, some recent reports have indicated that introduction of functional groups or heteroatom induces more strain in carbon materials. Therefore, introduction of atoms with larger atomic size than carbon into carbon materials may cause higher strain at their edges and thereby facilitate charge localization and associated chemisorption of oxygen. In other words, structural strain in doped carbon materials may be one of the dominant reasons for ORR activity enhancement [26]. The above inconsistent conclusions may be due to the scarcity of studies in this field and variation in experimental conditions, the mechanism of ORR activity enhancement is complicated and it may be different for different dopants, and further research work is therefore required.

#### 4. Conclusion

As can be seen from the above discussions, the use of doped carbon nanomaterials as ORR catalyst has become a significant research topic. Recent developments in the syntheses of doped carbon nanomaterials with well-defined macroscopic and microscopic structures have accelerated to a great extent the applications of the doped carbon catalysts in fuel cell. However, the present metal free doped carbon catalysts are still far from satisfactory for large-scale practical applications. Some scientific and technical problems still need to be solved, and deeper studies are thus required.

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